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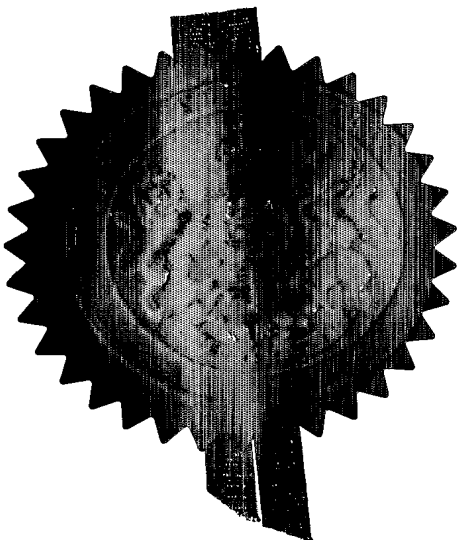
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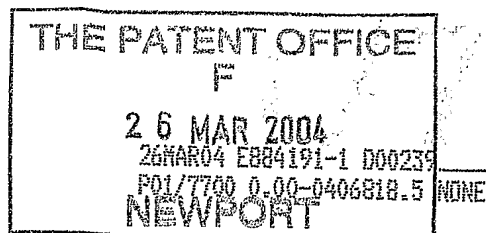


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26 MAR 2004

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The University Court of the University of St. Andrews
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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

40494700 B.5

4. Title of the invention
Steam Electrolyser

5. Name of your agent (if you have one)

Cruikshank & Fairweather MARK S. CLARK

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Description 9

Claim(s) -

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STEAM ELECTROLYSIS

The present invention relates to hydrogen production, and more particularly to hydrogen production by high temperature steam electrolysis with improved efficiency and reduced cost.

5

Hydrogen is becoming an increasingly important fuel. Various processes have been developed for producing it including inter alia, steam reforming of natural gas and by coal gasification, and water electrolysis. Existing processes do, however, suffer from various disadvantages including relatively low efficiency and high production costs.

10

It is an object of the present invention to avoid or minimize one or more of the above-mentioned disadvantages.

15

It has now been found that by using a proton conducting electrolyte membrane, which is substantially non-permeable to oxide ions and to molecular gas, and is stable at high temperatures, it is possible to dissociate water into hydrogen and oxygen and at the same time separate the hydrogen from the oxygen.

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Thus in one aspect the present invention provides a method of producing hydrogen comprising: providing a steam feed stream, contacting said steam feed stream with a proton conducting membrane supported on a porous redox stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a cathode coupled to the other side of said membrane so as to dissociate at least part of said feed stream therebetween, into protonic hydrogen and oxide ions at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.

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In another aspect the present invention provides a steam electrolyser for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

It should be noted that in the simplest case the anode may simply form part of the substrate adjoining the membrane where a suitable substrate is employed i.e. where the substrate material is electrochemically active. Alternatively the anode may comprise a thin layer of a different material interposed between the membrane and the substrate support.

With the present invention the hydrogen production process is substantially simplified, whilst having a relatively high efficiency, and uses apparatus of relatively economic construction. The process provides hydrogen gas which is free from oxygen, steam and other gases, thereby avoiding the need for any downstream separation of gases. Also the electrolysis and separation out of hydrogen gas, may be achieved without the need for any expensive precious metal catalysts or the like.

Various proton-conducting materials are known in the art which are stable to a greater or lesser extent at high temperatures. In general steam electrolysis is carried out at temperatures of around 900 to 1000 °C. A particular

advantage of the present invention is, however, that steam electrolysis can be carried out at significantly lower temperatures, for example, from 500 to 700 °C, whereby the materials and construction used may be significantly
5 simplified and reduced in cost. In general suitable proton-conducting materials comprise a material which allows the reversible dissociation of water into its lattice to form mobile protonic carriers therein. Such materials are frequently oxygen deficient perovskites of formula ABO_{3-d} .

10

Particular preferred materials which may be mentioned include $BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY10), $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$ (SCZTO) and $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$ (BCN18), as well as composites of such materials. Thus, for example, there may be used a membrane
15 comprising a layer of BCY10 which has relatively high electrochemical performance (in terms of proton conduction) in contact with the substrate, with an outer protective layer of SCZTO which has better stability - especially against chemical degradation by atmosphere CO_2 .

20

As indicated above, it is also important that the membrane should be substantially impermeable to molecular gas. Accordingly the membrane material needs to be in a substantially dense, non-porous, form. The membrane is also
25 substantially impermeable to oxide ions.

In order to maximize the efficiency of the electrolyser, the resistivity of the membrane should be kept as low as possible. Desirably therefore the membrane should be as thin
30 as is reasonably practicable. Preferably the membrane thickness is not more than 25 μm , advantageously from 1 to 25 μm , most preferably from 3 to 15 μm .

It is also important that the membrane should remain stably
35 attached to the substrate support under the high temperature

operating conditions of the electrolyser. Various methods are known in the art for forming thin films on substrates including inter alia: sol-gel techniques in which a liquid suspension is applied to a substrate, dried and then cured; 5 tape casting in which the membrane material is provided in a powder form embedded inside a polymer tape which is placed on the surface of the substrate and heat treated to form a substantially continuous film of membrane material; vacuum deposition in which the membrane material is provided in a 10 powder form suspended in a liquid carrier is placed on the surface of the substrate and drawn into the surface thereof by means of a vacuum applied to the remote side of the porous substrate, and then heat treated to form a substantially continuous film of membrane material at the substrate 15 surface; etc. It will be appreciated in relation to such processes that, in accordance with normal practice, the particle size of the membrane material applied to the surface of the porous substrate should not be significantly less than the pore size of the substrate, in order to minimize 20 penetration of the particles into the interior of the substrate. Using such techniques we have successfully obtained proton conducting ($\text{Sr}_3\text{CaZr}_{0.5}\text{Ta}_{1.5}\text{O}_{8.75}$) membrane films on porous conductive substrates (NiO:YSZ and LSM) with film thicknesses in the range from 3 to 100 microns, 25 depending on the number of layers deposited.

Various porous electrically conducting materials which are stable at the elevated temperatures used in steam electrolyzers are already known in the art, and may be used 30 for the substrate support in the present invention. Suitable materials generally comprise a metallised ceramic or a mixed conductive oxide having an electrical conductivity of not less than 10 Scm^{-1} , preferably not less than 100 Scm^{-1} , at the operating temperature of the steam electrolysis. Particular 35 suitable substrate materials which may be mentioned include metallised ceramics such as $\text{Cu:Al}_2\text{O}_3$ or mixed conductive

oxides such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), chromium-doped LSM (i.e. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$) or $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ (LSCF).

As indicated above, the substrate support requires generally
5 to be sufficiently porous to facilitate penetration of the
steam molecules to the membrane and to facilitate exhaustion
of oxygen molecules exiting from the membrane. In general
therefore the pore size should be not less than $0.5\text{ }\mu\text{m}$, and
conveniently from 0.5 to $10\text{ }\mu\text{m}$. Desirably the porosity is
10 from 30 to 60 %, preferably from 40 to 50%. Where such a
discrete anode is provided between the membrane and the
substrate, it will be appreciated that in such cases the
membrane is supported indirectly by the substrate. Generally
in such cases the anode layer is deposited on the substrate,
15 and then the membrane layer deposited onto the anode layer.
Various techniques are known in the art, including those
described elsewhere herein, for producing thin film layers
onto substrates of various kinds.

20 As noted above, a thin layer (generally 10 to $100\text{ }\mu\text{m}$,
preferably 30 to $50\text{ }\mu\text{m}$) of the substrate support itself may
conveniently function as the anode of the electrolytic
apparatus, (where the substrate material is electrochemically
active), and is connected to the voltage supply via a porous
25 metal current collector in generally known manner. A porous
cathode requires generally to be sufficiently porous to
facilitate exit of hydrogen molecules from the membrane. In
general therefore the pore size should be not less than $0.5\text{ }\mu\text{m}$,
and conveniently from 0.5 to $10\text{ }\mu\text{m}$. Desirably the
30 porosity is from 30 to 60 %, preferably from 40 to 50%. The
cathode may be provided on the surface of the membrane

electrolyte by painting, screen printing or sol-gel coating, and is connected to the voltage supply via a porous metal current collector in generally known manner. Suitable cathodes are conveniently of a transition metal such as porous metallic platinum or palladium, or a Ni cermet of a transition metal and a proton conducting electrolyte. Various mixed conducting oxides which may also be used, are known in the art including perovskite oxide materials such as those disclosed in WO2004/013925.

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One of the benefits of the invention is that the lower working temperatures allow the use of less expensive current collector metals such as steel, which may, if desired, be provided with electrically conducting protective film

15 coatings, e.g. of chromium.

(as well as avoiding the use of expensive precious metal catalysts etc).

The substrate supported membrane, electrode, and current collector, assembly may be electrically insulated from the gas supply and exhaust pipes and any external housing, which are generally made of metal e.g. steel, by means of a high temperature glass ceramic such as barium silicate or a high temperature cement.

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As indicated above the steam electrolysis may be carried out at a range of different temperatures. It will also be understood that higher temperatures have the advantage of reducing the direct electrical energy input required. It is, however, a key feature of the present invention that it allows the use of lower temperatures than have been used heretofore in steam electrolysis, which in turn allows the use of significantly more economic materials and forms of construction. It is also important to avoid using higher

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temperatures as these can result in oxide ion conductivity developing in the membrane and even permeability to water molecules. Preferably there is used an operating temperature of from 400 to 800 °C, most preferably from 500 to 700 °C.

5

In general it is convenient to use a steam supply at a temperature substantially equal to the desired operating temperature at the membrane. It is also possible though to supply steam at a lower temperature and to heat the substrate supported membrane, e.g. using an external electrical or fuel gas (conveniently hydrogen), furnace.

10

It will also be understood that the voltage required to be applied across the membrane for a given hydrogen flux will depend on the electrical resistance of the membrane, and any supporting substrate employed. The electrical resistance will in turn depend on the particular materials used, as well as the thickness thereof, and the operating temperature used. It is accordingly desirable that the membrane should be as thin as is reasonably practicable i.e. whilst still maintaining gas tightness and structural integrity under the operating conditions used. Typically we have found that useful levels/rates of electrolysis may be obtained with an applied voltage of the order of 1.1 to 1.2 V when using a proton conducting ($\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$, etc) membrane having a thickness of around 25 μm .

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The feed stream may be supplied to the electrolysis apparatus at ambient pressure. Steam generators, though, generally provide steam at super-atmospheric pressures and the use of such higher pressures - typically up to 10 bar or even 100 bar - has the advantage of increasing efficiency.

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The steam feed stream is generally supplied to the module via piping connected to the module so that the feed stream is passed across the surface of the substrate and undissociated

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steam together with oxygen produced are then carried away. At the cathode side, hydrogen gas produced is also generally exhausted by suitable piping. The piping (and conveniently also any external support such as a manifold or housing, for the substrate-supported membrane) may be made of any material known in the art but may conveniently be of steel or alumina, or the like.

The steam feed stream is generally contacted with the substrate support, by passing a flow thereof across the exposed surface thereof.

Further preferred features and advantages of the present invention will appear from the following detailed description given by way of example of some preferred embodiments described with reference to the accompanying drawings in which:

Fig.1 is a schematic section through a steam electrolyser module of the invention; and
Fig.2 is a schematic perspective view of a manifold interconnector for a multi-module electrolyser.

Fig.1 shows a steam electrolyser module 1 of the invention mounted in a manifold 2 and coupled to gas flow pipes 3,4 at cathode and anode sides 5,6 thereof, respectively. In more detail, the module 1 comprises a 5 μ m thick dense non-porous proton-conducting membrane 7 of BCY10 or BCN18 deposited on a 2 mm thick LSM substrate 8 having a 40% porosity and a pore size generally in the range of from 0.5 to 5 μ m.

On the outer face 9 of the membrane 7 (remote from the substrate support 8) is provided a porous metallic platinum cathode or hydrogen electrode 10, on top of which is provided a steel mesh current collector 11 connected 12 to the negative pole 13 of a DC voltage supply 14. At the anode side outer face 6 of the substrate 8 is provided a steel mesh

current collector 15 connected 16 to the positive pole 17 of the DC voltage supply 14 so that a positive voltage is applied to a thin (30 μm thick) layer 18 of the substrate 8 adjacent the membrane 7, which functions as an anode or steam electrode. The module 1 is electrically insulated from the steel manifold 2 and pipes 3,4 by a high temperature barium silicate glass ceramic seal 19.

The anode side pipe 4 has an inlet branch 4a through which high temperature steam 20 is fed in and passed across the exposed anode side outer face 6 of the substrate 8. Any undissociated steam 21, together with oxygen 22 produced by the electrolytic dissociation of the steam feed, are exhausted by an outlet branch 4b of the anode side pipe 4. The cathode side pipe 3 is used to exhaust hydrogen gas 23 liberated at the cathode 10.

In use of the above module the following processes occur:

at the anode $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$
20 at the cathode $4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2$

Fig. 2 shows part of a large scale steam electrolyser comprising a manifold interconnector 24 mounting multiple modules 1 such as those of Fig. 1.

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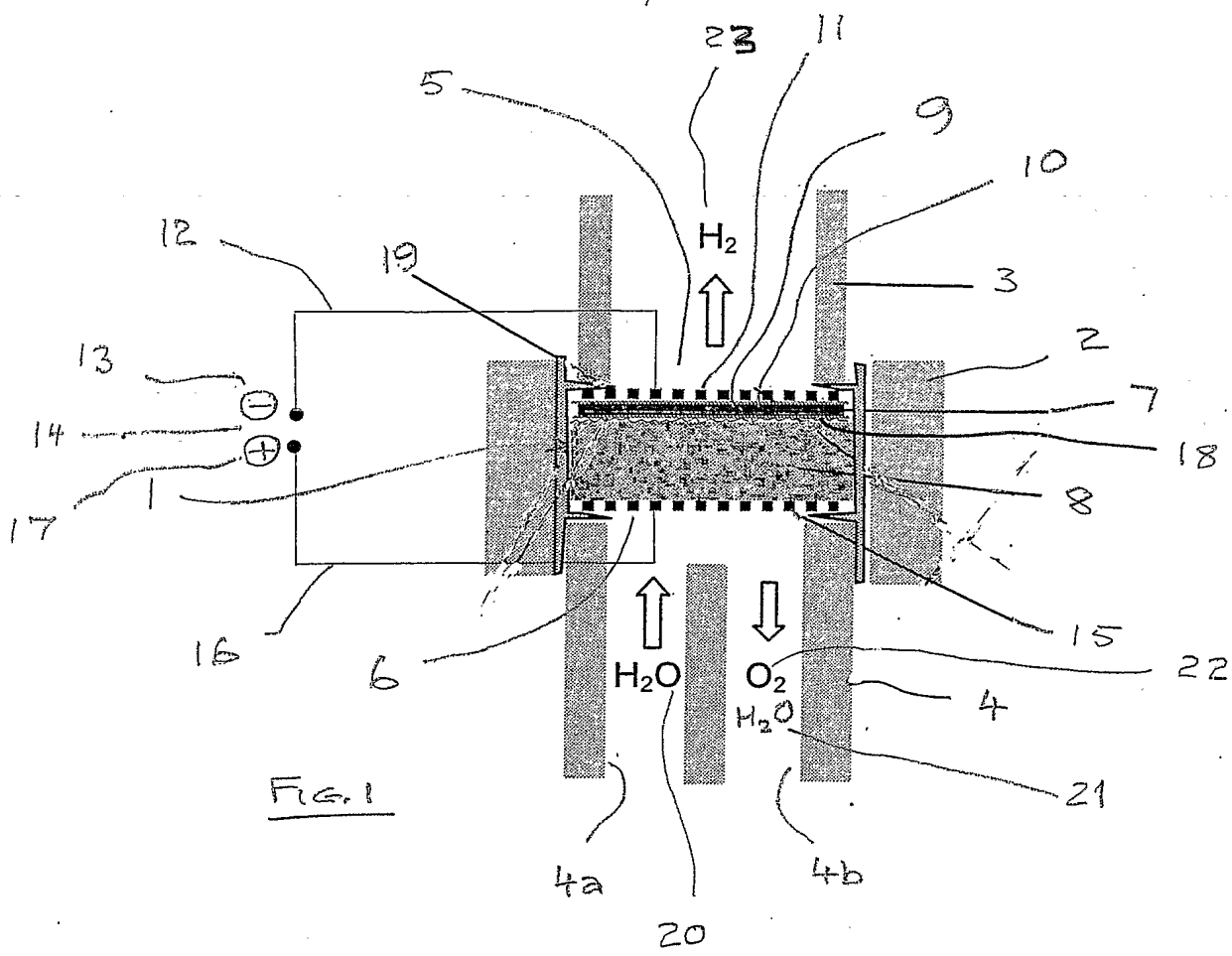


FIG. 1

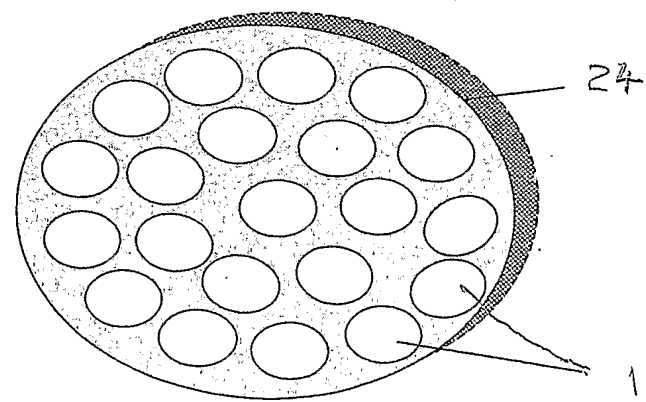


FIG. 2